THE ATOMIC WEIGHT OF TUNGSTEN.

BY EDGAR F. SMITH AND FRANZ F. EXNER.

(*Read April 7, 1904.*)

LITERATURE.

Berzelius, *Pogg. Ann.*, *8*, 1 (1826); Schneider, *Jr. prakt. Chemie*, *50*, 152 (1850); Marchand, *Ann. Chem. Pharm.*, 77, 261 (1851); Borch, *Jr. prakt. Chem.*, *54*, 254 (1851); Riche, *Jr. prakt. Chem.*, *69*, 10 (1857); Dumas, *Ann. Chem. Pharm.*, *113*, 23 (1860); Bernoulli, *Pogg. Ann.*, *111*, 573 (1860); Scheibler, *Jr. prakt. Chem.*, *83*, 324 (1861); Roscoe, *Ann. Chem. Pharm.*, *162*, 368 (1872); Waddell, *Am. Chem. Jr.*, *8*, 280 (1886); Pennington and Smith, *Z. f. anorg. Chem.*, *8*, 198 (1895); Smith and Desi, *Z. f. anorg. Chem.*, *8*, 205 (1895); Shinn, Thesis, University of Penn'a (1896); Schneider, *Jr. prakt. Chem.*, *53*, 283 (1896); Hardin, *Jr. Am. Chem. Soc.*, *19*, 657 (1897); *ibid*, *21*, 1017 (1899); Thomas, *Jr. Am. Chem. Soc.*, *21*, 373 (1899); Taylor, Thesis, University of Penn'a (1901).

The literature pertaining to this subject covers a period of nearly three-quarters of a century. Eight different methods have been used in striving to solve the problem. They are:

1. REDUCTION OF TUNGSTEN TRIOXIDE.

> Berzelius (2).
> Schneider (5).
> Marchand (2).
> Borch (7).
> Dumas (8).
> Bernoulli (6).
> Persoz (2).
> Roscoe (3).
> Waddell (5).
> Schneider (3).
> Shinn (4).
> Hardin (29).
> A total of 78 reductions.

2. OXIDATION OF METAL.

> Schneider (3).
> Marchand (2).
> Borch (2).
> Bernoulli (4).
> Roscoe (2).
> Pennington and Smith (9).
> Schneider (3).
> Hardin (37).
> A total of 62 oxidations.

3. WEIGHING THE WATER FROM THE REDUCTION OF TRIOXIDE.

> Riche (2).
> Smith and Desi (6).

4. DETERMINATION OF THE WATER CONTENT OF BARIUM METATUNGSTATE.

> Scheibler (5).
> Hardin (2).

5. ANALYSIS OF TUNGSTEN HEXACHLORIDE.

> Roscoe (2).

6. ANALYSIS OF IRON TUNGSTATE.

> Zettnow (4).

7. ANALYSIS OF SILVER TUNGSTATE.

> Zettnow.

8. DETERMINATION OF THE WATER IN SODIUM TUNGSTATE.

> Thomas (22).

The results obtained by the first and second methods are the most numerous. The frequent employment of these methods would indicate the opinion to be general that they are the most rational. This they are, notwithstanding the want of concordance evident in the work of all chemists who have pursued either one of these methods in the attempt to solve the existing problem. Their sufficiency has been doubted, especially by Hardin, working in this laboratory. He was disposed to attribute the lack of agreement in

his work to volatilization of substance, both in the experiments of reduction of trioxide and in those in which the metal had been oxidized.   Hardin adopted the method of purification pursued by Pennington and Smith, and therefore believed that the material with which he operated was pure ; hence the errors were the result of imperfections in the method employed.

Pennington and Smith, cognizant of the presence of molybdenum in the tungsten compounds, confirmed by numerous observations of others, were induced to undertake a solution of the difficulty surrounding the atomic weight of tungsten because they noticed in Schneider's communication, that when he reduced tungsten trioxide in a current of hydrogen " ein weissliches Sublimat " appeared on the anterior portion of the reduction tube, which sublimate Schneider thought was tungsten chloride, but which Pennington and Smith, in the light of the discovery of molybdenum in all tungstates, believed was due to the latter element.   They accordingly purified a portion of tungsten trioxide by the plan recommended by Schneider and, after eliminating any possible molybdenum content, made tungsten metal and oxidized it.   They gave as a result of their labors probably the most concordant series of figures ever published for the constant in question.   The other striking feature of this series was their high value, namely *184.921*.   This was much higher than that generally considered to be the correct value.   Its rise was supposed to be due to the complete removal of molybdenum.   Let it be noted that Pennington and Smith used tungsten metal from trioxide reduced in a crucible of platinum, and further that they used the second method only.

The work of Smith and Desi, who used the third method, apparently confirmed the conclusions of Pennington and Smith.   It may be said that the early work of Schneider, leading to the value *184*, had been practically confirmed by subsequent investigators, so that the constant *184* had been looked upon for a period of forty-five years as the accepted atomic weight of tungsten.   The experiments of Pennington, Smith and Desi could not fail to be regarded with some question notwithstanding the evident care exercised by them in preparing suitable material for their respective studies, and the conscientiousness to detail exhibited in the experimental work. Schneider was still living on the appearance of the communications just referred to and in letters to one of us, as well as in a public print, naturally took exception, in the most courteous man-

ner, to the methods and to the conclusions of those who advocated the higher value (184.92). It is not necessary here to enter into a detailed review of Schneider's second and later paper. Briefly, he very much doubted whether it was the complete removal of any molybdenum content from the tungstic acid which occasioned the rise in the atomic number. He also entertained grave doubts as to whether, in the methods employed, there were not sources of error which escaped these chemists. The small quantities of material used by Pennington, Smith and Desi were, in the opinion of Schneider, contributory sources of error.

The problem, attracting new attention to itself in this laboratory, led to further studies upon this subject, chief among which were the painstaking investigations of Hardin, extending over several years. Reference to these will show that few points of inquiry escaped this investigator, and one can readily comprehend the spirit which prompted him to say in his final contribution on this subject :

"So far as known there is no perfectly reliable method for the determination of this constant. The method of reduction and oxidation is probably more accurate than any of the other methods which have been employed. The results obtained by it vary about one unit and even more in exceptional cases."

In our frequent discussions on this topic, it did seem as if search for new methods was absolutely required ; that these alone might be expected to settle the difficulty once for all. Taylor, engaged at the time in this laboratory upon the ammonium tungstates, noticed that ignited tungsten trioxide, when dissolved in a solution of pure sodium carbonate, left a white flocculent residue. When dissolved in potassium hydroxide, this residue was not so evident, and in his thesis (University of Penn'a, 1901) he continues :

"On standing a few hours in sodium carbonate, this residue turned reddish-brown. On treatment with hot concentrated hydrochloric acid, it (having been previously washed) broke down into tungstic acid, and the filtrate contained the chlorides of iron and manganese. To ascertain if the original ammonium tungstate would reveal the presence of these impurities, it was dissolved in water, feebly acid-uiated with hydrochloric acid, and ammonium sulphocyanate added. No coloration was produced. Another portion of the solution was boiled with hydrochloric acid, the tungstic acid precipitated, and now the filtrate easily showed the presence of iron.

"The residue, insoluble in sodium carbonate, appears to be a tungstate of iron and manganese, which probably existed in the

ammonium salt, as an ammonium iron-manganese tungstate. Laurent[1] states that the mother liquor from ammonium tungstate contains such a salt. He ascribed to it the formula: $[12(NH_4)_2O, 6MnO, 2Fe_2O_3, 3H_2O, 45WO_3, 81H_2O]$.[2]

"Borch[3] analyzed this salt with the following results: WO_3 84.4%, $(Fe_2O_3 + Mn_2O_3)$ 4.6%, NH_3 4.0%, H_2O 7%. Laurent states that this complex salt is soluble in water and ammonia, and is peculiar in that ordinary reagents do not show the presence of iron, manganese or tungstic acid; further, that the salt is only broken down by prolonged boiling in acids or alkalies, and then the ingredients can be readily detected.

"Schneider[4] recognized the presence of this salt in ammonium tungstate, and stated that it was not removed after five or six recrystallizations. Also that it could not be removed by the ammonium sulphide treatment, for slight amounts of the sulphides of iron and manganese are soluble in the tungsten sulpho-salt. Berzelius[5] stated that the sulphides of tungsten, iron and manganese form a compound which is partly soluble in water.

"To remove this complex salt Schneider, purified his material in the following way: Tungstic acid, obtained from the sulpho-salt of tungsten, was boiled in *aqua regia*, and washed in acidulated water till free from iron. This was dissolved in dilute ammonia, and the solution precipitated by boiling hydrochloric acid, the resulting tungstic acid boiled in *aqua regia* and again washed. This oxide was again dissolved in ammonia and again precipitated. After reprecipitating three times in this manner, tungsten trioxide was obtained free from iron. However, on dissolving the oxide in potassium hydroxide, a slight brown residue remained which had escaped all earlier tests. This he assumed was not enough to affect the result of his work.

"Had he applied the sodium carbonate test, this residue would have been larger. In the recent repetition of his work,[6] he used material purified in precisely the same manner (in fact some of the original material), with the exception of the treatment for the elimination of molybdic acid.

"Borch[7] recognized this complex salt, and tried to remove it by fusion with potassium carbonate.

"Later investigators seem not to have appreciated the difficulty of eliminating it. It crystallizes in part with the ammonium tungstate, and can scarcely be entirely removed by recrystallization.

[1] *J. prakt. Ch., 42*, 126 (1847).
[2] *Comptes rendus, 31*, 693 (1850).
[3] *J. prakt. Ch., 54*, 254 (1851).
[4] *J. prakt. Ch., 50*, 152 (1850).
[5] *Pogg. Ann., 8*, 279 (1826).
[6] *J. prakt. Ch., 161*, 288 (1896).
[7] *J. prakt. Ch., 54*, 254 (1851).

Ignition of the ammonium salt, and resolution in ammonium hydroxide will not eliminate it. Nor will ammonium sulphide remove it. In fact it seems likely that it has never been wholly extracted from any previous material.

"The purification by Pennington and Smith[1] did not remove it, for though closely following the method outlined by Schneider, and adding to it the complete elimination of molybdenum, they omitted the final repeated precipitations with acid.

"To understand the effect of possible impurity, the following table is given. A molecular mixture of tungsten and the impurity is treated as though it were all tungsten, and the resulting atomic weight calculated.

Molecular Mixture.	*Reduction Series* *Atomic Weight.*	*Oxidation Series* *Atomic Weight.*
W + W	184	184
W + Mo	140	140
W + 2Fe	148	148
W + 3MnO	298	298
Loss of Material	Low	High

"A consideration of these numbers shows that: molybdenum and iron would produce a low value; manganese a high value; volatility a low value on reduction and a high value on oxidation. The error introduced by manganese is more than three times as costly as that introduced by iron, and more than two and a half times that introduced by molybdenum. These ratios would apply regardless of the proportion of the mixture.

"From these considerations it is believed, that the presence of manganese and iron will account for the high oxidation values, for their presence would affect the result in a twofold manner: Manganese through its inherent molecular changes $[Mn_3O_4 \leftarrow \rightarrow 3MnO]$, and iron through its secondary action on the volatility. Further, that the presence of iron, molybdenum, manganese, and volatility will explain the numerous discrepancies noted in the published work on this subject. Again, since iron and molybdenum decrease the value, and manganese and volatility increase the value, and iron and molybdenum influence the volatility, it is quite possible that such a mixture of these factors might occur that the errors would be compensated.

"Viewed in this way there still remains the necessity for determinations with material from which every trace of molybdenum, iron, and manganese, together with other possible impurities, has been removed.

"The method of determining atomic weights from the loss of carbon dioxide has been applied to a number of the elements. Its application to tungsten, and the special modification of the method necessary for accurate determinations has not been before recorded.

[1] *Proc. Am. Philos. Soc.*, *33*, 332 (1894).

Svanberg[1] and Struve fused molybdenum trioxide with potassium carbonate and determined the loss in weight. Their value is nearly six units too low and the method must be considered inaccurate. This method was tried with tungsten trioxide and gave values ranging from 160 to 180. The disadvantages of the method are that: the union takes place with considerable spattering; the temperature of fusion is so high that loss by volatility is probable; the alkaline carbonates when held in fusion slowly lose traces of carbon dioxide; and the resulting fusion is extremely hygroscopic.

"These difficulties may be obviated by combining the oxide and sodium carbonate in aqueous solution, and then expelling the water. Operated in this manner the method possesses promising value; and has numerous advantages, among which may be mentioned
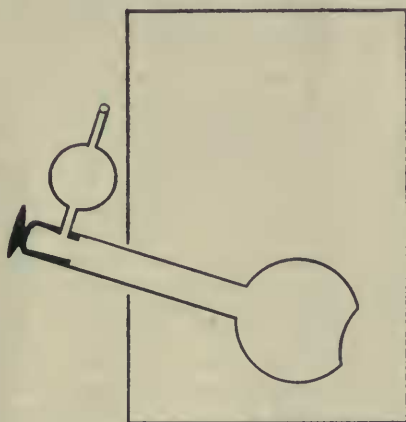
that: carbon dioxide has a molecular weight of forty-four, giving a value for comparison nearly as great as in the simple reduction and oxidation method; the union of sodium carbonate and tungsten trioxide in aqueous solution takes place at a low temperature, and the highest temperature used in the desiccator is a safe distance below the melting point of sodium carbonate, so that there is little chance for volatilization either of sodium carbonate or tungsten trioxide, and in the device used there is no chance for loss by spattering; large quantities of material may be combined with as much ease as small; the method itself would serve for a test of the purity of the material; the presence of chlorides, sulphates, sodium silicate, and potassium carbonate would not affect the result. The presence of alkaline hydroxides would; and to prevent the possibility of this, pure sodium carbonate was saturated in solution with carbon dioxide, and the resulting bicarbonate heated in a vacuum at 300° for three hours.

[1] *J. prakt. Ch.*, *44*, 301 (1848).

"The tungsten trioxide and sodium carbonate were combined in a glass bulb as in the sketch. A neutral glass is desirable for this purpose, and the bulb should be made of Jena glass, which will withstand the action of alkaline carbonates better than ordinary glass. If sodium carbonate dissolves the glass no error will be introduced, but if carbon dioxide be liberated through such solution, then the glass cannot be used. To determine this point a blank experiment was made, which showed that the total weight of the bulb and sodium carbonate remained unchanged, while 0.0017 grams of glass were dissolved; hence no appreciable evolution of carbon dioxide occurred. However, to prevent any possibility of such loss, a platinum bulb had better be used.

"It was found that moist sodium carbonate could be heated to a constant weight, by heating for one and a half hours at a temperature of 300° in a vacuum; and in this bulb the weight after standing several days remained unchanged. To insure complete desiccation the bulb was always heated double the required length of time. A water pump was used to produce the diminished pressure, and since nothing can be perfectly dried in a vacuum resulting from such a pump, a calcium chloride tower was introduced. But calcium chloride will not perfectly desiccate a gas, so that phosphorus pentoxide had better be used. However, for the preliminary experiments in hand, calcium chloride was sufficient.

"The method of procedure was as follows: some sodium carbonate was introduced into the bulb and heated for three hours at 300° in a vacuum. The suction was disconnected, and after cooling, the combined weight of bulb, sodium carbonate, and dry air was obtained. Tungsten trioxide was then introduced through a long funnel, the bulb was exhausted, allowed to fill with dry air and again weighed. This gave the weight of tungsten trioxide. The weight of the sodium carbonate, further than being present in excess need not be known. Water was added and the bulb heated in a glass air bath, so that the course of the reaction could be watched. The mixture slowly effervesced, and when the action had ceased the vacuum apparatus was attached, and the water distilled off. This water was tested and found to be neutral. The calcium chloride tower was now introduced, and the residue, consisting of a mixture of sodium tungstate and carbonate, was heated for three hours at 300° in a vacuum. After cooling and thus allowing the bulb to fill with dry air, it was detached and weighed. This loss in weight gave the carbon dioxide evolved. It may be added that the entire bulb should be inside the air bath, until the water has been removed; and then the upper portion be placed outside and the temperature increased to 300°. In this way no moisture will condense in the head, and the stopper remaining perfectly dry will not become jammed. The stopper should not be lubricated.

"The following results were obtained, from impure material,

which in the previous experiments in this paper gave values ranging from 182.24 to 184.82, and which was known to contain iron, maganese, and probably molybdic acid :

	Weight of Na_2CO_3 grams.	Weight of WO_3 grams.	Weight of CO_2 grams.	Atomic Weight of Tungsten.
(1)........2.7		2.0802	0.3952	183.60
(2)........2.3		2.1937	0.4173	183.30
(3)........3.5		4.0818	0.7762	183.38
(4)........3.8		3.3629	0.6394	183.41

"These numbers, in that they indicate the atomic weight of tungsten, are worthless; in that they show promise for the new method, are of value. The presence of impurity would lower the result; what value the method will give for pure material can only be conjectured."

Taylor's experience re-emphasized the absolute necessity of satisfying ourselves beyond every reasonable doubt that the material for the atomic weight determinations was pure; at least as pure as the means at hand would furnish. The admission of Schneider that his purest substance contained traces of impurity, insoluble in caustic potash, and Taylor's discovery that every sample of tungsten trioxide tested by him gave a residue, insoluble in sodium carbonate, made us very solicitous regarding the purity of all material which had been used in any previous investigations, for it will be found upon consulting the literature that almost every experimenter was content to proceed with ammonium paratungstate which was perfectly white in color. Three to five recrystallizations were held to be sufficient to attain that condition.

Our doubts became so overwhelming that it was decided to begin the work anew with the mineral wolframite and to ascertain, once for all, what it contained in order that search might be made for all such constituents, and every effort put forth to insure their perfect removal from the salts which might be experimented upon. Accordingly, in the summer of 1901 large quantities of wolframite, from Lawrence County, S. D., were decomposed and the resulting tungstic acid converted into ammonium paratungstate. The mother liquors from the salt were black in color and gave in due time the interesting compound—ammonium vanadico-phosphotungstate—described by us in the *Jour. American Chemical Society, 24,* 573. Its discovery added, of course, vanadium and phosphorus to the list of possible contaminating substances: columbic oxide, silica,

molybdic oxide, ferric oxide, manganese oxide, etc. Large amounts of ammonium paratungstate were taken for the purification of the tungsten trioxide by methods which may now be presented.

Method 1.—This first fraction was collected apart, dissolved in distilled water and recrystallized ; the first crystallization was again set aside and dissolved, this operation being repeated ten times. A portion of the sixth crystallization was ignited in a platinum crucible and the resulting oxide was digested on a water-bath with a 2% solution of sodium carbonate free from iron. The oxide dissolved, but its solution was quite turbid. Upon standing, a white residue settled out, which after washing with water and decomposition with a few drops of hydrochloric acid showed tungstic acid and iron. Portions of the tenth recrystallization behaved similarly. The mother liquors, including that from the tenth crystallization, assumed a dark-brown coloration upon concentration, indicating thereby that not only iron, but that also the vanadico-phospho-tungstate, already alluded to, continued with the ammonium tungstate. Vanadium too was found in a portion of the tenth crystallization when it was heated in an atmosphere of hydrochloric acid gas. Hence it was concluded that this method was unsatisfactory and it was abandoned. Chemists, who in the past were content to look upon ammonium paratungstate as being very pure when its color was perfectly white (and from published statements most have been content with this criterion), which it is after the third or fourth crystallization, cannot have had pure substance for their investigations, hence the fluctuation in their results is easily comprehended.

Method 2.—This may be called the method of Borch. In it the mineral was fused with sodium carbonate, the fusion exhausted with water and after filtration the liquid was precipitated with calcium chloride. The resulting calcium tungstate was filtered, washed and decomposed with hydrochloric acid. The liberated tungstic acid was dissolved in ammonia water and the ammonium salt crystallized out. The method was carried out with rigid adherence to the printed instructions, but it proved entirely unsatisfactory.

Method 3.—Solutions of ammonium paratungstate, decidedly brown in color, were boiled with precipitated calcium carbonate. Ammonia and carbon dioxide were evolved, while calcium tungstate was precipitated. The solutions lost nothing in color. After

filtering out and washing the calcium tungstate it was boiled with hydrochloric acid. Tungstic acid of a rich yellow color separated. It was washed and dissolved in ammonia water. There was a very slight bluish-colored residue. The ammonium paratungstate, which crystallized out, was perfectly white in color, but a portion of it ignited and the resulting oxide, digested with a dilute sodium carbonate solution, disclosed the usual white residue in which tungsten and iron were found.

The salt, purified in this way, was fully as free from impurities as a salt which had passed through six crystallizations from water. This fact led us to prepare pure calcium carbonate and hydrochloric acid before repeating the method with another portion of ammonium paratungstate.

Commercial calcium carbonate was boiled with a solution of pure ammonium chloride. Iron and other impurities remained with the excess of calcium carbonate. The filtrate from the latter was precipitated with pure ammonium carbonate. The resulting calcium carbonate was thoroughly washed and then dried.

Ordinary hydrochloric acid was saturated with calcium chloride and after the addition of phosphorus pentoxide was distilled with water. This gave pure acid. With these purified reagents ammonium paratungstate, which had passed through several crystallizations, was subjected to the treatment outlined in the beginning of this section. The purified salt, when tested, showed but traces of impurities and it is very probable that these, after several repetitions, would disappear entirely. The actual trial was not made, because another course seemed to lead to the desired end in a much shorter period. Experience also showed that nitric acid was preferable.

Method 4.—In this procedure a boiling solution of ammonium paratungstate was decomposed with hydrochloric acid. The precipitated tungstic acid was again dissolved in ammonia and the decomposition repeated. Repeating this process several times yielded tungstic acid which might be asserted to be quite pure, although when the mother liquors from the several fractions of the ammonium salts were reduced to a small volume the dark color appeared. A white residue, although slight, was also obtained from the ignited tungsten trioxide. Wyman (Thesis, University of Pennsylvania, 1902) found, after twenty-five decompositions with hydrochloric acid, evidences of similar contamination. This

chemist tried seven different schemes in his endeavor to obtain pure tungstic acid without the desired result. Accordingly, on resuming this part of our study in the summer of 1902 we determined to eliminate every possible source of contamination from the various reagents which we proposed using. Thus, fifteen liters of hydrochloric acid were purified as already described. It was free from every impurity, which was proved by carefully repeated tests. Eighteen liters of nitric acid were distilled after the addition of pieces of pumice and some sodium hydrogen phosphate. The product left no ponderable residue when a definite volume of it was evaporated to dryness in a platinum vessel. The sodium carbonate was made pure by fusing it in a platinum vessel and introducing into the molten mass a small quantity of pure, precipitated calcium carbonate which dissolved; the mass being held for five minutes in the liquid state. After cooling, the fusion was allowed to dissolve out in cold water. The calcium carbonate, iron, etc., were filtered off and the solution evaporated to crystallization. The sodium carbonate which separated was recrystallized four times. Platinum vessels were used for the purpose. They are essential. Portions of the purified salt were examined for silica and iron, and their absence demonstrated. There was now every reason to believe that the reagents, including the water (for it had been redistilled), were pure. They contained nothing which would contaminate the tungsten trioxide. Therefore, if the latter left a residue upon digestion with a dilute sodium carbonate solution, that residue plainly came out from the tungstic oxide.

And now we must digress a little. Wyman experienced difficulty and annoyance in his efforts to dissolve tungstic acid in ammonia water. Others have had, doubtless, similar experiences. There invariably remains a bluish-white mass which no amount of ammonia or protracted boiling eliminates. More than a kilogram of this substance had accumulated from Wyman's work and came into our possession. Its bluish-green tint suggested the presence in it of some reduction product, probably occasioned by the hydrochloric acid. We accordingly projected the mass into boiling concentrated nitric acid. A violent evolution of chlorine immediately followed and continued until the material had acquired a rich yellow color. Whence came the chlorine? More of the blue residue was dried at 100°, then heated upon a platinum foil. Great volumes of ammonium chloride were expelled, leaving pale-yellow

colored tungsten trioxide. An analysis of a portion of the dry, bluish material was made, when 5.48% of NH_4 and 9.65% of Cl were found. The presence of this amount of foreign substance could only be accounted for on the assumption that in the liberation of tungstic acid from ammoniacal solutions of ammonium tungstate with hydrochloric acid portions of the latter and of the ammonium chloride were so combined that no amount of washing would remove them. They are retained, and firmly, by the tungstic acid. Let those who question this examine the white, slimy residue which appears on attempting the solution of tungstic acid in ammonia. Most of us have quieted our consciences on this point by asserting that such residues are "those persistently insoluble paratungstates." If the solution from such residues be reprecipitated with hydrochloric acid quantities of insoluble bodies again appear. These are beyond question ammonium chlorinated tungstic acid derivatives which even prolonged boiling with concentrated acids will not change to the yellow acid. They merit further study.

The preceding experience emphasized the necessity of removing all the ammonium chloride in tungstic acid if the precipitation method of purification was to be pursued. This was done in the following way: two to three liters of concentrated nitric acid, diluted with water to half their volume, were heated in a large porcelain dish until it began to fume strongly, when 25cc. of pure hydrochloric acid and three kilograms of dry and fairly pure ammonium tungstate were added. Vigorous action set in and volumes of decomposition gases escaped. The mixture was constantly stirred during the operation. As soon as the action diminished, ten to fifteen cubic centimeters of pure hydrochloric acid were introduced at intervals. As the decomposition approached completion, the yellow tungstic acid lost its porous character and collected as a heavy granular powder upon the bottom of the dish, but it was heated with occasional stirring for a period of from three to four hours. At the expiration of that time, there remained only tungstic acid and nitric acid with traces of chlorine and ammonia. The tungstic acid was washed by decantation with pure distilled water until the tungstic acid suspended in the solution subsided very slowly, and the wash-water from it showed but a faint acid reaction. The subsided yellow-colored acid was placed in a porcelain dish, hot distilled water was poured over it and ammonia was conducted into the solu-

tion. As a rule all of the acid dissolved, and there was at the most a very small residue. Thus forty-five liters of a saturated solution contained a residue which weighed less than two grams.

The ammonium paratungstate separating from such a solution showed the needles and plates characteristic of that salt. Only the first three fractions were preserved. They represented seven-eighths of the entire substance. The other portions were set aside. A second and a third treatment, as outlined above, was given the first three fractions, and when the salt, finally obtained, was subjected to the sodium carbonate test, allowing the solution to stand over night, it remained absolutely clear. The mother liquor from the salt, reduced to five cubic centimeters, remained colorless. One object in this long and baffling study had at last been obtained. We were the possessors of seven hundred grams of pure ammonium paratungstate.

Three kilograms of impure ammonium paratungstate were decomposed by acids as described above, the operation being repeated five times, when the ammonium salt from the last decomposition responded admirably to the crucial tests. This salt disclosed none of the substances which were found accompanying the tungstic acid originally, hence the latter was considered pure and was applied as will appear in subsequent paragraphs. However, before proceeding further it seems proper to direct attention to certain other experiences which possess interest and value.

The Residue Obtained by Digesting Tungsten Trioxide with Sodium Carbonate.

Ammonium paratungstate, after three crystallizations and when quite white in color, was ignited in a platinum crucible. Two hundred grams of oxide were obtained in this way and were digested with a 2% solution of sodium carbonate of excellent commercial quality. Quite a residue appeared. It was washed and dried. A portion, weighing 0.4712 gram, was digested with *aqua regia*. The insoluble part weighed 0.4309 gram, while the solution of the soluble constituents, weighing 0.0403 gram, was reduced to a small volume, diluted with water and precipitated with ammonia. The iron weighed 0.0337 gram as ferric oxide. Manganese and platinum were also found. The tungsten trioxide, when digested with hydrofluoric acid, lost 0.0149 gram, representing silica. Or, if the results be tabulated, they show:

Weight of residue	0.4712 gram.		......
" " WO_3	0.4160 "		88.28%
" " SiO_2	0.0149 "		3.16 "
" " Fe_2O_3	0.0337 "		7.15 "
Manganese, platinum, etc.	Undet.		......
			98.59%

Even pure sodium carbonate will not remove all of the impurities, although it may serve to test the purity of the oxide as to the iron, etc., which may be present.

IGNITION OF AMMONIUM PARATUNGSTATE.

The ignition of this salt in platinum vessels, as ordinarily conducted, contaminates the trioxide with platinum.   To minimize this contamination a platinum crucible was fitted tightly two-thirds of its length into an asbestos board.   A platinum wire shaped into a tripod was set upon the bottom of the crucible.   A smaller platinum crucible was supported by the tripod.   Into the latter were introduced from time to time not more than from two to three grams of ammonium tungstate.   A red heat was applied to the outer crucible.   The ammonia was expelled in the course of half an hour, when the crucibles were covered with an inverted porcelain lid, it being lifted from time to time to admit air.   Constant weight was obtained in two hours.   This procedure gave the best results which could be gotten by the use of platinum crucibles.   While the oxide is cooling it should be protected from all reducing atmospheric dust, because the hot oxide is extremely sensitive to the action of such substances.   This is evident from the following : a platinum rod previously heated in a flame and applied to the hot oxide produces no change, but if the rod be touched quickly to the skin and then laid on the hot oxide, a green spot will appear at the point of contact.

The efforts to substitute silver and gold crucibles for those of platinum demonstrated that these metals, too, were appreciably absorbed by the oxide.   Porcelain crucibles were used, notwithstanding the absorption of silica, which would of course become greater as the time of ignition was prolonged and as the heat was increased.   Further, the oxide in immediate contact with the porcelain invariably showed a green color.   The glaze of the crucible always indicated etching.   With an unglazed crucible the action was not so evident, hence the contamination was not so great, and the most satisfactory results were gotten by setting the

unglazed porcelain crucible in a platinum crucible and bringing about the ignition of the salt in this double-walled chamber. The coloration of the surface of the oxide was extremely slight. Experience, however, eventually showed that the best course to pursue consisted in digesting the ammonium paratungstate directly in a porcelain casserole with pure nitric acid and a few cubic centimeters of hydrochloric acid until it was completely decomposed, and the ammonia and hydrochloric acid were destroyed. When the tungstic acid was evaporated to complete dryness, it showed a rich orange-yellow color. It was transferred to an unglazed porcelain crucible and there ignited gently for half an hour. This may be done over a direct flame, the crucible being covered with an inverted porcelain lid. Any enclosed nitric acid was expelled by the gentle heat, and the weight soon became constant. The resulting tungstic oxide had a uniform yellow color. Green was absolutely absent. This procedure eliminated the reduction caused by the ammonia, and it may be added that by its use glazed crucibles were employed every day in similar ignitions for several weeks without showing the least etching or corrosion of the surface.

Having at last gotten pure salt and pure oxide, the question arose as to what method should be adopted in the determination of the atomic weight of the metal. The method proposed by Taylor (p. 130) was new. The results he obtained were with material not especially purified, yet their fair agreement pointed to the possibility of arriving at a definite value with the pure substance, such as was now available. Preliminary trials were executed according to Taylor's suggestions, using glass apparatus just as he had done, and drying at 400° to constant weight. The weighings were all made on the same day and under uniform conditions. The main purpose was to ascertain whether concordance in results could be realized. The results in the subjoined table show the opposite:

	Na_2CO_3	WO_3	CO_2	At. Weight
1.............	5.9 gm.	2.45645 gm.	.46775 gm.	183.07
2.............	5.6 "	2.72292 "	.51785 "	183.36
3.............	5.5 "	3.32953 "	.63288 "	183.48
4.............	4.7 "	3.96720 "	.75473 "	183.29
5.............	4.0 "	3.44944 "	.65489 "	183.75
6.............	4.1 "	3.41273 "	.64796 "	183.74
7.............	4.8 "	6.10309 "	1.16087 "	183.32
8.............	3.9 "	6.39735 "	1.21044 "	183.39
9.............	3.5 "	2.17450 "	.41332 "	183.48
10.............	3.1 "	1.57903 "	.29966 "	183.85

The trioxide used in experiments 1 to 4, inclusive, was obtained by gently igniting the ammonium salt in a porcelain crucible. That used in experiments 5 and 6 was strongly heated in a porcelain crucible. In ·7 and 8 the ammonium tungstate was heated for one hour in a double platinum crucible. The oxide in experiment 7 had been heated two hours in the same kind of crucible, while in experiment 10 the ignition continued for two hours in the double platinum crucible. The gradual rise in the value to 183.85 by protracted heating could surely not be due to the expulsion of volatile matter, for there was no change in weight after the first hour of ignition in the double crucible. Evidently the oxide absorbed impurities which led to the rise in the atomic weight. Accordingly, samples of ammonium paratungstate were ignited under conditions as nearly similar as possible in crucibles of platinum and of porcelain. The values from the oxide in the crucibles of porcelain were higher than those from the oxide made in platinum crucibles, showing in all probability, that the oxide took up more foreign material from the porcelain than from the platinum. Therefore, the mere ignition of the ammonium salt in vessels such as have been described drew in sources of error. These would, of course, have to be eliminated if the method was to be tested upon its own merits. It was sought to accomplish this by igniting thoroughly dry ammonium paratungstate and ascertain the loss (water and ammonia) sustained by different amounts, which resulted in discovering that the percentage of volatile matter could be obtained to within less than 0.01%, which would answer for the purpose of atomic weight determination. And therefore, in the actual experiments, the ammonium paratungstate was weighed out directly into the flask, it being only necessary to make the proper calculations to arrive at the amount of trioxide which was thus used. Six determinations were made; the results in the atomic value varied from 183.4 to 183.81. The early explanation for the lack of concordance, if the method was not faulty, would be to suppose that the action of the soda upon the glass would withdraw varying amounts of silica, and there would follow, of course, the liberation of corresponding amounts of carbon dioxide. If this really occasioned the error, it was hoped that the substitution of a platinum bulb, similar to the glass vessel, would lead to success. This was done. The experiments were performed as before, with slight modifications where it was considered advisable and advantageous. The atomic

values in a series of five trials ranged from 182.85 to 183.64. Patient search was made for the reason, every step being tested repeatedly, until eventually the conclusion was forced upon us that carbon dioxide, in varying amounts, was disengaged through the decomposition of the sodium carbonate in the final drying. Jacquelain (*Jahresb.*, 1860, p. 116; *A. Ch.* [4] 28, 86, and *A. Ch.* [3] 32, 205) showed that this salt loses from 0.03 to 0.05% in weight at 400°, and other observers have shown that the loss continued with the length of the period of ignition and with the temperature. Here, then, was a serious defect in the method which would explain why the values found were low, and why they differed so widely. The attempts to correct this weak point proved futile, so that the method, having had a thorough trying-out, was abandoned after months of arduous work.

It was hoped that perhaps a normal silver tungstate might be made, which after solution in potassium cyanide could be electroyzed and the value of tungsten obtained from a comparison with the precipitated silver. Fifteen experiments were made. In one series (the best) of five experiments the results varied from 184.00 to 184.39. It was found, after much search, that there could be no certainty as to when a normal salt was really in hand. Washing and drying, even when performed with the utmost care, occasioned a change in the character of the salt. The method was discarded.

An effort was also made to obtain a cadmium salt of definite composition. Much time was given to it, and experiments were made in the electrolysis of bodies believed to be uniform in composition. The atomic values ranged from 181.90 to 185.71.

Having subjected three new methods to vigorous tests in our efforts to solve the problem along new lines, and having found them utterly deficient, the hope still remained that possibly some of the earlier methods might with pure material give satisfactory results. The writers felt, without meaning to reflect in the slightest upon earlier investigators, that their material possessed the merit of superior purity; and if that were really the case, older methods, simple in principle and easy of execution, might well be expected to give concordant values. Of the 175 experiments made by the entire corps of previous investigators, there is but one short series, namely, that of Pennington and Smith, in which there is that degree of concordance which is desirable and necessary in fixing the

atomic value of any element. Splendid as is the work of Schneider, worthy as it is of high praise, there still remains the fact, not to be pushed aside, that between the minimum and maximum values there is a difference of more than a unit. The atomic value given by Schneider, Hardin and others for tungsten is 184—the mean of very widely differing series. Cognizant of these facts, with faith in the greater purity of our material, steps were taken to repeat several older procedures.

PREPARATION OF TUNGSTEN HEXACHLORIDE.

Chlorine, free from oxygen and moisture, is absolutely essential to obtain this compound pure and in comparatively large amounts. The product must also be sublimed repeatedly in an atmosphere of chlorine, without exposure to the air. The first condition, although apparently simple, is really very difficult to attain ; and after much experimenting, we cannot say that we got chlorine absolutely free from moisture. But the quantity of oxychloride formed along with the hexachloride may be taken as an index of the amount of moisture (also oxygen) in the chlorine.

The generator was charged with material sufficient to yield chlorine an entire day without the addition of acid and consequent introduction of air into the apparatus. When the flow of gas commenced to grow less only the gentlest heat was applied for a few minutes to the generator. The chlorine was most completely dried by conducting it through three six-inch U-tubes connected in series, containing pumice stone saturated with pure concentrated sulphuric acid, and in the bend sufficient acid to fill the bottom of the tubes, thus causing the gas to bubble through the acid before each new preparation. Indeed, it was about every fourth day that a renewal was made. Only traces of oxychloride were observed. The reaction of chlorine and metal took place in a combustion tube of soft glass, 15 to 18 mm. in diameter and 4½ feet in length. The tube was contracted in two places to the thickness of a lead pencil, thus making three sections, of which the first was 3 feet in length, the second 1 foot and the last ½ foot. A porcelain boat carried the tungsten metal. The chlorine was passed through the apparatus for two hours before any heat was applied. This was done to expel the air. Then the burners of the furnace (to within three of the boat) were lighted, beginning with those most distant from the boat, the flames being small. The tube beyond the boat

thus reached a temperature of nearly 350° C. These burners were then extinguished, while those immediately beneath the boat were lighted, the flames being small. The tube to a length of eight inches beyond the boat was also heated. In a very short time the reaction began, noticeable at first in the yellow vapors which condensed in the colder part of the tube, beyond the furnace, to the light brown oxychloride. This did not continue more than two minutes, when copious reddish-brown vapors appeared and condensed beyond the lighted burners to brilliant blue-black needles. The formation is very rapid. The utmost vigilance is constantly required to the very conclusion of the experiment. In two hours twenty grams of metal may be fully converted into hexachloride. That portion of the combustion tube at which the hexachloride condenses should be kept just hot enough to cause the traces of oxychloride to pass beyond the hexachloride. This can be readily adjusted after a little experience. When working with large amounts the deposits of the hexachloride may obstruct the tube. In that event manipulate a lamp flame with the hand beneath the chloride until it is partially melted. This converts it into a compact solid, requiring less space. Melting and resublimation of the chloride removes every trace of oxychloride. Two sublimations are sufficient for the purpose. The tube can then be sealed off at the contracted points. Perfectly pure hexachloride has a beautiful, brilliant steel-blue color. It can be readily transferred to clean, dry weighing bottles and preserved in them. It has marked stability. There is no perceptible action on bringing the chloride into water at the ordinary temperature even after considerable time. On the application of heat the decomposition does not begin until the temperature of the water reaches 60°. The specific gravity of the hexachloride, taken in water at the ordinary temperature, equaled 3.518. After all the weighings were made the water employed for the purpose was tested with litmus; it gave the very faintest acid reaction. Having obtained in the above manner large quantities of the hexachloride, it was decided to change it to trioxide and thus arrive at the atomic weight of the metal. Roscoe had determined the chlorine in this compound. His results were not especially concordant. Perhaps this was due to the involved method or to the presence of traces of oxychloride· However, our thought was to adopt the simplest available course, hence we aimed to convert the chloride into oxide. Roscoe has

stated that when hexachloride is directly decomposed with water and the resulting acid ignited to oxide, the latter will contain chlorine which cannot be expelled by heat. We had hoped to pursue this method, but as it had the condemnation of so high an authority the hexachloride was introduced into freshly distilled ammonia water, contained in a weighed platinum dish, with the expectation of eventually getting ammonium tungstate and chloride which would leave the trioxide upon ignition. Experience showed that the quantity of the resulting ammonium chloride was so great that even with the most careful ignition there was much danger of expelling mechanically appreciable amounts of the oxide. Nor was it forgotten that it is very doubtful whether from such a mixture the chlorine could be completely removed by heat.

The treatment of the hexachloride directly with nitric acid was also found impracticable.

In spite of Roscoe's objection to the decomposition with water it was believed that the transposition could be carried out. Five glazed No. 2 porcelain crucibles of 40cc. capacity were selected, thoroughly cleansed and ignited, allowed to cool in vacuum desiccators and weighed upon a specially constructed Troemner balance, sensitive to $\frac{1}{10}$ of a milligram. There was next introduced into each one of them tungsten hexachloride from a weighing bottle which was reweighed after the removal of each portion. The crucibles with their chloride content were placed on water-baths and cold distilled water introduced into each. When the volume of water was insufficient for the quantity of chloride sufficient heat was generated by the reaction to make the water boil and spattering followed. At 60° the decomposition proceeded quietly to the hydrated trioxide, which at the beginning had a slight greenish-yellow color, due probably to imperfect decomposition, as mentioned by Roscoe, but this tint disappeared as the hydrochloric acid was expelled. When the mass was perfectly dry a few drops of pure concentrated nitric acid was introduced from a pipette upon the trioxide. Instantly any green tint vanished and was replaced by a rich orange-yellow color. The excess of nitric acid was slowly evaporated away and the oxide assumed a pale yellow hue.

The crucibles were now removed from the water-bath, and after careful drying were ignited for half an hour to a dull red heat, then allowed to cool in the desiccator, and at the expiration of an hour and a half were weighed.

In the calculations the values for oxygen and chlorine were taken at 16 and 35.45 respectively. The specific gravity of tungsten trioxide was found to be 7.157 and that of tungsten hexachloride 3.518.

Seven different series of determinations were made, each from a different sample of hexachloride. The results appear in the subjoined table :

No. of Exp.	No. of Series.	Wght. of WCl₆ Cor. for Vac. in grams.	Wght. of WO₃ Cor. for Vac. in grams.	At. Wght. of W.	Means of Series.	Mean of Means.
1	I.	3.18167	1.86085	184.04	184.01	
2		2.66612	1.55903	183.94		
3		3.52632	2.06244	184.05		
4	II.	1.52117	0.88972	184 07	184.04	
5		1.22299	0.71523	184.00		
6		2.28445	1.33603	184.01		
7		3.25404	1.90337	184.10		
8		3.37078	1.97133	184.01		
9	III.	7.76488	4.54082	183.98	183.98	
10	IV.	2.08764	1.22114	184.11	184.08	184.04
11		2.80141	1.63859	184.09		
12		3.24328	1.89681	184.02		
13		4.97975	2.91262	184.06		
14		3.04036	1.77838	184.10		
15	V.	4.31046	2.52133	184.10	184.06	
16		2.21201	1.29381	184.07		
17		2 70368	1.58135	184.06		
18		3.60658	2 10934	184.03		
19		2.63037	1.53835	184.02		
20	VI.	3.41668	1.99808	184.07	184.04	
21		3.49940	2.04675	184.06		
22		3.86668	2 26145	184.05		
23		3.40202	1.98970	184.03		
24		3.20661	1.87533	184.01		
25	VII.	3.26386	1.90909	184.09	184.06	
26		6.73833	3.94031	183.94		
27		7.37889	4.31643	184.14		

It should be mentioned here that at the conclusion of these experiments etching or corrosion of the glaze of the crucibles could not be observed. Nor was there any stain upon them; they looked as if they had been unused.

METALLIC TUNGSTEN.

It would be superfluous to set forth here the steps taken in procuring the metal. They are familiar to every reader. They were identical with those described by Hardin. One point, however, is worthy of notice. It was discovered that if the trioxide, reduced to metal, had been previously gotten by the ignition of ammonium paratungstate in vessels of platinum, then it might well be expected that after the removal of the tungsten from the reduction boats the latter would show dark spots here and there. This occurred, but uncontaminated trioxide was repeatedly reduced in porcelain by hydrogen without leaving dark stains.

Several experimenters—Riche, Desi, Shinn and Hardin—endeavored to reach the atomic value of tungsten by collecting the water resulting from the reduction of definite amounts of trioxide in hydrogen. Their results were disappointing in the extreme, although the method is surely rational and in some measure ideal. The reasons for its failure have never been satisfactorily explained. We were induced to give it trial. Every attention to detail was scrupulously observed. The results were most disappointing, and yet we cannot give a reasonable explanation for our failure. There seems to be an inherent defect in the method which we were unable to lay bare.

We also reduced definite quantities of trioxide to metal, and from the loss in weight sought to get the atomic value of tungsten. Again the results were discordant. The boats were never stained from the reduction, nor was the porcelain tube in which the reduction took place stained, but on close scrutiny particles of metal could be seen along the sides of the tube. They rested loosely upon it and were removed with ease. This metal, in all probability, was carried out into the tube by the aqueous vapor produced in the reduction. This is, therefore, a serious point in this method.

There remained, finally, only method 2, another time-honored method, upon which much discredit had been cast. Yet with pure material it seemed worth the while to give it further trial. The metal used in this study was made from trioxide obtained from the hexachloride. Portions of it were weighed out into the same crucibles which had been used in the experiments with the hexachloride and gently heated with air contact. The steps in the

ignition were those which any careful analyst would observe, so that they need not be mentioned here. The final oxide was uniformly yellow in color throughout its entire mass.

The weighings here, as in all previous experiments, were reduced to vacuum standard. The value of oxygen was placed at 16. The specific gravity of the oxide was, as before, 7.157, and that of the metal —19.

In the appended table it is to be understood that each single series was made from portions of the same sample of metal. The results are:

No. of Exp.	No. of Series.	Wght. of W. in gms.	Wght. of WO$_3$ in gms.	At. Wght. of W.	Means of Series.	Mean of Means.
I	I.	2.24552	2.83144	183.96	183.96	
2	II.	1.78151	2.24619	184.07	184.07	
3	III.	1.63590	2.06270	183.98	184.04	
4		1.38534	1.74665	184.04		
5		1.29903	1.63774	184.09		
6	IV.	2.01302	2.53781	184.12	184.09	
7		2.18607	2.75632	184.01		
8		2.36755	2.98478	184.12		
9		1.94958	2.45781	184.12		
10	V.	4.43502	5.59141	184.09	184.10	184.065
11		2.37603	2.99548	184.11		
12		2.58780	3.26260	184.08		
13		2.58503	3.25886	184.14		
14		2.38298	3.00441	184.06		
15	VI.	2.05578	2.59169	184.13	184.11	
16		3.60828	4.54915	184.08		
17		6.22621	7.84949	184.11		
18	VII.	5.28444	6.66239	184.08	184.08	
19	VIII.	3.99095	5.03138	184.12	184.12	
20	IX.	7.30166	9.20647	184.00	184.00	
21	X.	3.44143	4.33870	184.10	184.08	
22		2.67709	3.37541	184.01		
23		4.96735	6.26229	184.13		

In series VII, a very large quantity of oxide was heated in hydrogen from 9 A.M. until 5 P.M. The resulting metal was placed over night in a desiccator, and on the following day a por-

tion of it was weighed out for the eighteenth experiment, the remainder being heated for a day more in hydrogen. After standing over night a second portion was removed and used in experiment 19. The remainder was exposed all of the third day to the action of hydrogen, and was then oxidized for experiment 20. Had not the first reduction been complete, the results would not have agreed so well.

The mean atomic value from the hexachloride is 184.04, that from the oxidation of metal 184.065, or the average of the two independent series is *184.05*, which probably approximates the truth very closely and may be safely regarded as the atomic weight of tungsten.

SUMMARY.

Our study, extended over so long a period, has revealed—

1. That it is quite doubtful whether any chemists who in the past occupied themselves with a determination of the atomic weight of tungsten have worked with pure substance. Tungstic acid is prone to form "complexes." It was found that if the acid contain no iron, for instance, but be digested with acids, *e.g.*, hydrochloric or nitric acid, in which iron is present, the latter will enter the tungstic acid. Iron and manganese are eliminated from the acid with the greatest difficulty. In the earlier work there is no evidence of their removal. Neither do we discover that vanadium and phosphorus had been considered as present, yet in purifying ammonium paratungstate by recrystallization alone it was found that the tenth recrystallization showed vanadium.

2. The slimy, greenish or bluish-white masses believed to be "paratungstates" because of their great insolubility are probably "complexes."

3. The fourth method of purification can be relied upon to yield pure tungstic acid.

4. The use of pure sodium carbonate (2%) to dissolve tungsten trioxide gives an excellent means of ascertaining when the iron, manganese and silica are fully removed, but that its development into a method for the determination of the atomic weight of tungsten is not at all probable.

5. The plan of digesting pure ammonium paratungstate with nitric acid, then evaporating to complete dryness and gently igniting affords pure oxide.

6. That porcelain vessels are preferable to those of gold, silver or platinum for the ignition of ammonium paratungstate and tungstic acid.

7. That the oxidation of metal (method 2) leads to reliable atomic numbers when the material is pure.

8. That tungsten hexachloride can be completely transposed into pure oxide with water and a little nitric acid.

The John Harrison Laboratory of Chemistry, University of Penna.

THE RIPENING OF THOUGHTS IN COMMON.

" Common Sense is Thoughts in Common."

BY OTIS T. MASON.

(*Read April 9, 1904.*)

Those who are entangled in official or commercial life, and, indeed, observant persons generally, will recall many instances in their daily experiences when they have mentioned a name only to see its owner appear. Or they have a friend, say, in the Straits Settlements. After a long silence they begin to worry about him and sit down to write to him. While they are thus engaged the postman hands in an epistle from Singapore signed with his name.

There is, of course, an element of chance in such coincidences. A vast number spring out of deep-seated, normal biological conditions. It is not here denied that many, associated with abnormal or hypersensitive conditions, are so startling in time and detail as to give rise to beliefs in telepathy.

Leaving out the causes just mentioned, this paper will be confined to those artificialities of life called culture, though the natural causes mix freely with these.

The purposeful actions of all humanity have become so artificialized as to make the natural, physical man subservient to the new man, the *Homo sapiens*. Racial activities and community experiences have entirely changed, so that coincidences in speech, manners, customs, and arts, however surprising they may be, are also due to the maturing of thoughts, desires and purposes held in